Nanowire Probes for Magnetic Resonance Force Microscopy

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論文内容要約

Magnetic resonance imaging (MRI) is well known as a powerful instrument for a visualizing three-dimensional structure inside a sample. However, the sensitivity and spatial resolution of the conventional MRI is limited by several tens to hundreds of micrometer scales due to limitations of conventional inductive detection techniques. In the early nineties, Magnetic resonance force microscopy (MRFM) combination with MRI and scanning probe microscopy (SPM) techniques is firstly invented by sidles, who also proposed the mechanical detection of a single spin. Comprehensive atomic-scale microscopy will exert a transformational impact in material science, nanoelectronics and microbiology. In order to realize the goal of single nuclear spin detection and atomic-scale resolution, great effort and persistence in theoretical and technical improvement are required. MRFM uses a high force-sensitivity probe with a magnetic tip to detect a force between a magnet and spins in the sample material while the spins are excited using magnetic resonance technique. A silicon nanowire probe is proposed that enable high force-sensitivity and response speed for MRFM application. The sensor, having shorter response time, is required because it takes much time from several tens of hours up to couple days for obtaining a three dimension image using current MRFM.

The first MRFM experiment demonstrating the MRFM principle is reported in 1992 (J.A. Sidle et al.), and involved the detection of electronic spin resonance (ESR) in diphenylpicrylhydrazil (DPPH). Shortly thereafter, two DPPH particles were successfully imaged in 1993 (O. Züger et al.). The next step involved transferring the expertise gained in the ESR experiments to the detection of nuclear magnetic spins. As the “magnetic moment of common nuclei are at least 650 times smaller than the moment of the electron”, the detection of nuclear spins is, in general, more difficult. Nonetheless, detection of nuclear magnetic resonance (NMR) via the MRFM principle is successfully performed. Paralleling the development of the ESR experiments, imaging of nuclear spins is later carried out. Obtained in a span of several years in the early 1990s, these results were all positive and reinforced the feasibility of single spin detection Motivation of electron or nuclear spins. In order to achieve single spin detection, the focus returned to electron spins. An improvement in the detectability of several orders of magnitude required countless improvements, among which is the fabrication of better cantilevers, a better understanding of the inversion and nutation of the electron spins, and spin relaxation effects.

Recently, researchers succeeded in detecting a single electron spin, two-dimensional imaging of nuclear spins with a spatial

resolution of 90 nm and three-dimensional images of individual tobacco mosaic viruses with a resolution better than 10 nm using MRFM technique. The last result, compared to conventional magnetic resonance detection methods that use inductive coils to sense nuclear spins, MRFM is about 100 million times more sensitive. However, reaching the ultimate goal of single-molecule imaging will require innovations that radically enhance the technique's sensitivity.

The basic idea behind MRFM is to sense the nuclear or electron spins in a sample by measuring the force that a magnetic field gradient exerts on these moments. Usually, this is achieved by having the magnetic force drive a small mechanical oscillator, such as a microfabricated cantilever. As a force detector, micro- and nanocantilevers are of great interest for a number of applications, such as magnetometry of nanoscale magnetic particles, femtojoule calorimetry, and various types of force microscopy. In particular, the proposed detection of single-spin magnetic resonance using MRFM requires the detection of forces in an attonewton (1 aN=10^{-18} N) range, which is much smaller than typical resolution of scanning force microscopy, i.e. approximately piconewton. Recent advances in fabrication of micro- and nanoelectromechanical systems (MEMS/NEMS) have allowed researchers to detect extremely small masses, forces, and displacements using a resonant sensor. Nanomechanical structures of a nanowire and nanotube have been proposed for next-generation mass and force sensors because of their small size and excellent material properties. In particular, silicon nanowires have been widely studied as a promising candidate in mass and force detection. In general, two techniques have been developed for fabrication of silicon nanowires such as bottom-up approach (Vapor liquid solid (VLS), oxide assisted growth (OAG), and metal assisted chemical etching and top-down approach. The bottom-up method is a growth or synthesized technique of the silicon nanowires from bulk silicon wafer either metal catalyzed-assisted or metal catalyzed-free. Meanwhile, top-down approach starts from bulk silicon wafer and scales down to the desired size and shape of silicon nanowires using a lithographic process. Generally, the fabrication of silicon nanowires via a top-down process which employed the application of advanced nanolithography tools on silicon-on insulator (SOI) is mostly compatible with conversional complementary metal oxide-semiconductor (CMOS) or nanomechanical resonator technology that typically consist of deposition, etching and patterning steps. Basically, the silicon nanowires fabrication started from the bulk material and scaled down into a single silicon nanowire or silicon nanowire array that can be formed with the help of nanolithography techniques such as electron-beam lithography (EBL), lithography patterned nanowires electro deposition, nano imprint lithography, and photolithography.

The purpose of this thesis is to develop a high force sensitive probe to detect attonewton force for MRFM at room temperature. In order to minimize the minimum detectable force of the silicon nanowire probe, a design model considering the geometry and fabrication of silicon nanowire having detectable force of attonewton-scale at room temperature, integration of silicon nanowire with a magnet and demonstration of force detection based on electron spin resonance (ESR) were performed.

One of the most important issues for sophistication is the force sensitivity and resolution of cantilever probes in MRFM. The force sensitivity may be systematically improved by fabricating cantilevers with (1) softening to reduce the spring constant, (2) weight lighting to increase the resonance frequency and (3) miniaturization to reduce the viscous drag from the environment and increase the Q factor, then equipping the magnet with (4) stronger magnetic field gradients and operating it at (5) low temperatures. Then, It have considered the minimum detectable force because the smallest force that can be detected by observing the deflection of a cantilever is limited by thermomechanical noise.

According to this equation of thermomechanical noise, it is found that a high Q factor, thin, narrow, and long probe structure such as a nanowire is desirable for detecting small force. It is found that the force sensitivity of 100 aN can be obtained in more than 20 kHz of resonant frequency with the spring constant below 10^{-2} N/m (Assumed 200 nm thickness and thickness, Q = 100000, T= 293 K). A mirror and a magnet support part is required to the real design of the nanowire probe at current MRFM device. The length from 30 μm to 92 μm of the nanowire probe with a mirror can achieve 100 aN or less of force sensitivity. We can also design for silicon nanowire with two types of magnets: a Ni thin film magnet and a Nd-Fe-B particle magnet. A smaller size of the magnet has higher magnetic field gradient, and force sensitivity is also higher. However, the size of magnet should be optimized according to a sample size because short distance of resonant slice which generated by the small magnet is limited to the detectable depth of the sample.

Silicon nanowire probes were fabricated by top-down process using silicon on insulator wafers having top silicon thicknesses of 100 nm and 200 nm. The width and length of the fabricated nanowires are 160 nm ~ 220 nm and 32 μm ~ 72 μm and the octagon mirror with 5 μm of the inradius is formed at the middle of the probe. Two different types (thin film and particle) of magnets are integrated at the end of the probe. The magnet formation on the nanowire probe is difficult to fix the magnet at the end of the nanowire. In this research, it is found that the magnet support part is required to fix the nickel magnet film at the end of nanowire design. Furthermore, the nanowire probe with the nickel magnet cannot be annealed to increase the Q factor because of nickel silicide formation. We have concluded that the nickel magnet is not suitable choice as a magnet material on nanowire probes of MRFM, which requires a high Q factor to detect small force. In order to increase the reflectivity for fine measurement of interferometer in MRFM system, the tungsten films is partially deposited on the silicon mirror. Since the intensity of interferogram should be increased with the metalized mirror, the deflection signal using the interferometer in MRFM system might be improved with lower noise level. Instead of the nickel magnet on the nanowire probe, a Nd-Fe-B magnet is putted on the end of probe using a manipulator. The anneal process has been successfully done, and the Q factor is increased as expected. To achieve ideal increment of Q factor by annealing, the mounting process of the magnet particles need to be optimized to avoid any contamination to the silicon nanowire probes.

As the first step of the characterization of the silicon nanowire probe, the resonance responses of three different lengths of nanowire probe with 32 μm, 52 μm and 72 μm were measured. The different resonant frequency and Q factor of the nanowire probes are observed. Both of values are decreased as their length increased. The force sensitivity is improved when the length of the probe is longer. When the Ni magnet is integrated on the silicon nanowire probe, the resonant frequency and the Q factor are decreased. Therefore, the force sensitivity became reduced from 5.3 times to 6.5 times by integrated nickel. Using the nickel thin film as a magnet for MRFM, there are two problems. The first issue is the difficulty to perform annealing process because nickel-silicide is formed by the reaction between nickel and silicon over 300ºC. The second issue is that the resonance slice is generated in a very short distance from the magnet. Thus, it is limited to measurable depth of sample.

With the Nd-Fe-B magnet, however, the force sensitivity with decreasing the resonant frequency and the Q factor are decreased from 87 aN/Hz$^{1/2}$ to 240 aN/Hz$^{1/2}$ about 2.7 times. Since the silicon nanowire probe with Nd-Fe-B magnet can be annealed and the magnet can be magnetized after the annealing process, the reduced Q factor can be restored by the post anneal process. Additionally, the generated resonance slice in MRFM measurement is forming at a sufficient distance to measure the samples with micron size. The Nd-Fe-B particle magnet is the most suitable material as the magnet on the nanowire probe instead of the Ni thin film magnet.

In order to obtain MRFM signals, the fabricated silicon nanowire probe has been installed in MRFM device. A scanning measurement of force map based on ESR for three-dimensional imaging of radicals has been demonstrated using the fabricated nanowire probe.

The force signal can be measured by the silicon nanowire probe with the Ni thin film magnet. Detected force is $1.3 \times 10^{-15}\ N/\sqrt{\text{Hz}}$ and force noise appears on even another part from slice with magnitude of $2.6\times10^{-16} N/\sqrt{\text{Hz}}$. Then, S/N ratio that is calculated in MRFM signal, is 5.

The experimental result of F_{min} using the fabricated probe with the Nd-Fe-B magnet is 82 aN/√Hz. The calculated spin density at the peak of 1.9 GHz is 4.6×10^{18} spins/cm^3. The estimated spin density: 1.5×10^{21} spins/cm^3. Calculated result is about 10^3 spins smaller than the standard value. This reduction of spins is possibly due to oxidation reaction with long-term air exposure. Typical three-dimensional MRFM data can demonstrating a sequence of two-dimensional scans from the magnet to a particle sample distances in 2 μm steps.

In order to evaluate the defects or radical distribution subsurface in the sample without destroying, thin film measurement system is also required. The method that lengthens the distance between the magnet and the mirror from 10 μm to 50 μm so that measurable area can be larger, for designing the probe the estimated thickness of the resonant slice is 220 nm and the calculated spin density is 4.1×10^{18} spins/cm^{3}at the peak. With only lengthening distance between the magnet and the mirror, it is possible to measure MRFM signal of thin film for certain area.

As the result, the Si nanowire probes have a high potential ability as a force sensor using in various instruments at room temperature. Fabricating the Si nanowire probes with magnet is expected to provide a high force resolution and response speed for force sensing and nanometric imaging, such as MRFM detection.